

IV.D.7 High-Temperature Membranes

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Objectives

- To develop new membranes and membrane electrode assemblies (MEAs) for operation at temperatures substantially in excess of 120°C

Approach

- Simultaneously carry out R&D on:
 - Physical chemistry of polymer electrolytes
 - New polymeric electrolytes
 - New approaches to proton transport in polymer electrolytes
 - Development of MEAs based on new polymer electrolytes

Accomplishments

Physical Chemistry

- Computational studies revealed key intermediate states in proton transfer processes; showed that water plays a role in ‘bridging’ and organizing acid groups to facilitate proton transfer

New Membranes

- Synthesized new polymers with higher acidity
- Developed several strategies targeting ‘water replacements’

Catalyst-Coated Membranes (CCMs)/Electrodes

- Successfully fabricated MEAs for one class of new membrane materials; achieved performance comparable to that of Nafion-based MEAs

Industrial and Other Collaborative Interactions

- Worked directly with several university partners in developing and testing high-temperature membranes
- Assisted DOE industry partners in CCM development for high-temperature membranes

- Developed draft Roadmap for High Temperature Polymer Membranes
- High-Temperature Polymer Membrane Working Group (HTPMWG) was expanded and strengthened through several meetings

Future Directions

- Perform more extensive computational studies on novel systems
- Continue to develop methods for screening new membrane concepts at a higher rate; test new electrolytes in fuel cells on a 4 month cycle starting in the fall of 2002
- Expand initial tests on enhancing electrode performance; develop capability for probing oxidation reduction reaction (ORR) at temperature ex situ; develop understanding of interactions at buried interfaces within electrodes
 - Develop reliable CCM fabrication approaches
 - Continue to develop means for scale-up of polymers, film-making and CCM production to modest scale
- Industry and Other Collaborations
 - Continue to make industrial and academic contacts from Case Western Reserve University (CWRU) to enable technology transfer and dissemination of ideas
 - Organize the HTMWG (streamline funding mechanism, improve meeting scheduling); evolve toward a discussion group format, idea exchange

Introduction

The need to operate at temperatures exceeding 100°C presents difficult new challenges for the polymer electrolytes used in fuel cells. This difficulty stems from the decrease in water content of the polymer electrolytes in the desired temperature range. There is a need for detailed understanding of the impact of poor or zero hydration on membrane and electrode processes in the fuel cell. Water plays a key facilitating role in proton transport; thus, lower water content leads to lower conductivity. Lack of water also has important negative consequences for electrode behavior.

Approach

At this point, we do not know which of several approaches is most promising. Thus, our membrane development efforts involve (1) a full-fledged effort to explore approaches involving polymer synthesis and development, as well as implementation of new “carrier” media to replace the function of water in Nafion, and (2) a study of proton transfer dynamics. We are using theoretical approaches to explore specific possibilities for new acid group types or for

acid-base interactions that could lead to progress in proton transfer media. We are also working to establish better understanding of the energetics of proton transfer to inform synthetic efforts. We also are working to incorporate new polymers in fuel cells by developing catalyst-coated membranes from the new materials. Finally, we have assisted DOE in setting up a range of polymer electrolyte development efforts, involving several universities and with significant industrial input.

Results

Physical Chemistry

As a starting point for our efforts, proton solvation and transfer in water-containing polymer electrolytes will provide some clues on critical steps in the approach. We are studying the energetics and dynamics of these processes. The tools we develop allow us to compare strengths of various target acids and assess the efficacy of water ‘replacements.’ We continue to expand the range of acid types studied as hydrates using density functional computational methods. These studies give us insight into the relative importance of solvation and dissociation

processes for various highly delocalized anions. The most interesting work this year used a sophisticated *ab initio*/molecular dynamics method to identify some surprising aspects of the proton transport dynamics. Specifically, we found that sidechain-to-sidechain hopping of protons could occur, albeit with the ‘cooperation’ of certain water configurations bridging between sidechain groups. This finding is highly suggestive regarding possible water replacements and their structural requirements for facilitating proton transport.

Additional work is underway to use computational methods to (i) tailor bases to mimic water, perhaps using substituted imidazoles or other proton carriers; (ii) understand proton transport in phosphoric acid/basic polymer systems; and (iii) augment other experiments on new polymers and additives of various types.

New Membranes

Three classes of membrane materials are presently in preparation and testing. These are (i) polymers and inorganic materials with controlled pore size to be modified with acid groups lining pores, (ii) polymeric systems with intrinsically stronger acid groups, and (iii) polymer systems swollen or imbibed with tailored proton acceptors. These are useful both intrinsically and as test or model systems. At least two more types of materials are ‘on the drawing board.’ Details of our ideas and approaches will be provided as the materials are tested later this year.

CCMs

We are forming CCMs from new polymers, often with radically different properties than those to which we are accustomed. Observed difficulties in achieving good performance with new CCMs stem from processes occurring at several different length scales:

- Macro scale (CCM level): adhesion phenomena, polymer segregation in catalyst layer, mechanical properties of electrode and membrane
- Meso scale (agglomerate level): mass transport of gases, continuous proton and electron conducting pathways

- Nano scale (local level): proton accessibility to site, electrocatalysis, polymer adsorption, polymer mobility

We have successfully catalyzed the Virginia Tech membranes and obtained performance comparable to that obtained with Nafion membranes of comparable thickness. Results are shown in Figures 1 and 2. The importance of these results lies in our ability to overcome difficulties inherent in catalyzing many of the emerging new membranes. Achieving good performance required some treatment of the CCM under operating conditions in the cell. The cells thus prepared appear to be robust in lifetests over hundreds of hours.

A more fundamental problem that arises in the high temperature regime is the necessity of good proton accessibility to electrodes. Many new polymer types proposed involve a sulfonated aromatic polymer. Microelectrode studies of the ORR on such materials indicate a significant loss of activity with decreasing water content in the polymer, far exceeding that observed with Nafion. This is likely due to the lower acidity of the aromatic sulfonates compared with that of the perfluorinated material. Our best results to date have been obtained using Nafion as the ionomer in the cathode catalyst layer.

We are actively studying the impact of the range of environments local and corresponding different

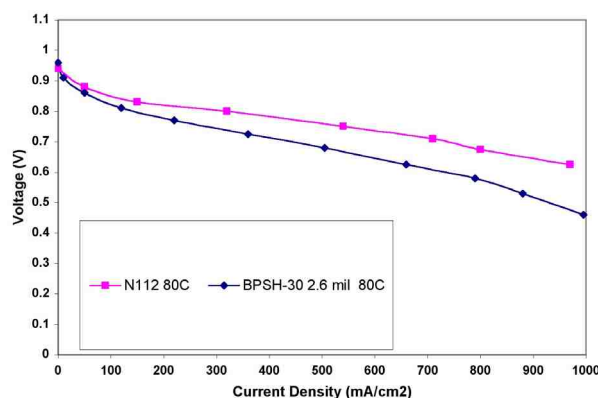


Figure 1. Polarization curves showing comparison of performance at 80°C of CCMs prepared from Nafion 112 and biphenyl sulfone (BPSH-30, 2.6 mil thick) membranes. Catalyst loading: 0.2 mg/cm² Pt anode, 0.4 mg/cm² cathode.

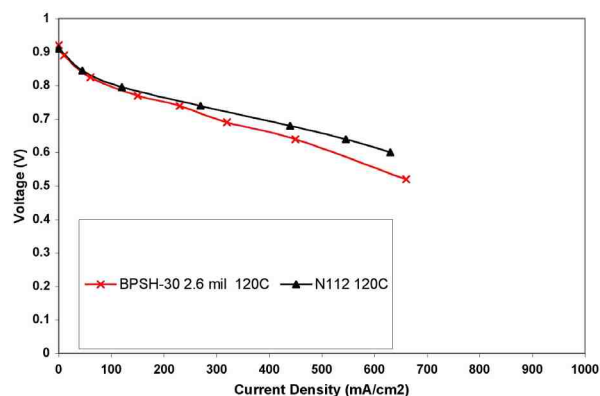


Figure 2. Polarization curves showing comparison of performance at 120°C of CCMs prepared from Nafion 112 and BPSH-30 (2.6 mil thick) membranes. Catalyst loading: 0.2 mg/cm² Pt anode, 0.4 mg/cm² cathode.

degrees of proton access to surface. Given the constrained dynamics of the polymer system, acid access to the catalyst surface is a key issue. Various additives, such as low molecular weight acids, have been and are being used to augment catalyst layer acidity and the mobility of acidic groups. Results to date have been inconclusive.

Industrial and Other Collaborative Interactions

We are engaged in a series of collaborative efforts with industry, national laboratories, and universities to facilitate efforts to achieve the targets for high-temperature polymer membranes. We have organized the High-Temperature Polymer Membrane Working Group, which has met four times to date. Bi-annual meetings allow us to assess progress and to communicate issues and needs to the high-temperature membrane community at large.

Conclusions

The development of new polymer electrolytes for operation at elevated temperature is under way. However, this is a long-term project. Replacement of water is the most difficult problem, but adequate stability and cathode activity are not trivial objectives to achieve. We have developed several different approaches to address this problem. Fundamental work, including computational and experimental studies of new acid-functionalized materials, can

provide useful insights into the conduction process to guide synthetic efforts. The first polymers geared for temperatures in excess of 100°C are emerging, and testing is showing that, although promising, there are definite shortcomings. Work on making viable new materials continues.